STUDY OF CHEMICAL OXYGEN DEMAND AND OIL-GREASE REDUCTION FOR SPENT CAUSTIC FROM KEROSENE TREATING UNIT IN PETROLEUM INDUSTRY WASTEWATER TREATMENT PLANT

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ABSTRACT

Spent caustic or used caustic soda is generated from the scrubbing process in the petroleum refinery industry. Treatment is needed for spent caustic because it typically has high chemical oxygen demand (COD) and oil-grease (OG) concentration that exceeded the limit of Department of Environment (DOE) regulations. In this study, the spent caustic were tested for its COD concentration by using a spectrophotometer and its OG concentration by using Standard 5520B, liquid-liquid, partition-gravimetric method. Then, the spent caustic was treated by using coagulation and flocculation method with aluminium sulphate as primary coagulant and activated carbon and soda ash as a coagulant aid. The optimum concentration of primary coagulant and coagulant aids was determined from Jar Test. The treated spent caustic was tested for its COD and OG concentration to determine the percentage of reduction of COD and OG concentration. It is found out that the COD concentration for untreated sent caustic is at a range of 12880-23800 mg/L and OG concentration at a range of 2285-6257mg/L. From this study, the optimum concentration of primary coagulant and coagulant aids are 200 mg/L of alum and 15 mg/L of both coagulant aids, which is activated carbon and soda ash that was able to reduce 58.15% of COD and 66.21% of OG concentration in spent caustic wastewater. The usage of coagulant aid reduced the amount of alum needed and increases the coagulation and flocculation efficiency. However, the treated spent caustic still does not meet the DOE requirement for Standard B, which are 10 mg/L for OG concentration and 100 mg/L for COD concentration. Therefore, coagulation and flocculation method alone are not effective in reducing the high COD and OG concentration in spent caustic, to meet with the DOE requirement. A pre-treatment or secondary treatment should be carried out along with coagulation and flocculation treatment method. The information obtained from this study is useful for scale up purpose in the petroleum refining industry that choose coagulation and flocculation method to treat spent caustic wastewater.

ABSTRAK

Sisa kaustik atau kaustik soda yang telah digunakan, dihasilkan daripada proses menyental dalam industri penapisan petroleum. Rawatan diperlukan untuk sisa kaustik kerana ia biasanya mempunyai nilai keperluan oksigen kimia (COD) serta minyak dan gris (OG) yang melebihi had yang ditetapkan oleh Jabatan Alam Sekitar (JAS). Dalam kajian ini, sisa kaustik telah diuji untuk menentukan nilai COD dengan menggunakan spektrofotometer manakala nilai OG ditentukan dengan menggunakan Standard 5520B , kaedah cecair-cecair, pembahagian-gravimetrik. Kemudian, sisa kaustik telah dirawat dengan menggunakan kaedah koagulasi dan flokulasi dimana aluminium sulfat digunakan sebagai koagulan utama manakala karbon teraktif dan abu soda sebagai koagulan bantuan. Kepekatan optimum koagulan daripada koagulan utama dan koagulan bantuan ditentukan daripada Ujian Balang. Sisa kaustik yang telah dirawat, diuji untuk nilai COD dan OG untuk menentukan peratusan pengurangan COD dan OG. Daripada hasil kajian, didapati bahawa sisa kaustik yang belum dirawat mempunyai nilai COD antara 12880-23800 mg / L dan nilai OG di antara 2285 - 6257mg / L. Daripada kajian ini , kepekatan optimum koagulan utama dan koagulan bantuan adalah 200 mg / L aluminium sulfat dan 15 mg / L bagi kedua-dua koagulan bantuan, iaitu karbon teraktif dan abu soda yang mampu mengurangkan 58.15 % nilai COD dan 66.21 % nilai OG dalam sisa kaustik. Penggunaan koagulan bantuan telah mengurangkan jumlah aluminium sulfat yang diperlukan dan secara tidak langsung meningkatkan kecekapan koagulasi dan flokulasi. Walau bagaimanapun, sisa kaustik yang telah dirawat masih tidak dapat memenuhi keperluan Jabatan Alam Sekitar bagi Standard B, iaitu 10 mg / L untuk nilai OG dan 100 mg / L untuk nilai COD. Oleh itu, koagulasi dan flokulasi sahaja tidak berkesan dalam mengurangkan nilai COD dan OG yang tinggi dalam sisa kaustik, untuk memenuhi keperluan Jabatan Alam Sekitar . Satu pra - rawatan atau rawatan sekunder perlu dilakukan seiring dengan kaedah koagulasi dan flokulasi. Maklumat yang diperolehi daripada kajian ini amat berguna untuk peningkatan skala dalam industri penapisan petroleum yang memilih kaedah koagulasi dan flokulasi untuk merawat air sisa kaustik.

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LIST OF SYMBOLS

mg/L	milligram per liter
%	percentage
g/L	gram per liter
°C	degree celsius
mL	milliliter
L	liter
mg	milligram
RPM	Revolutions Per Minute
NTU	Nephelometric Turbidity Units
kg/m^3	Kilogram per meter cubic

LIST OF ABBREVIATION

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DOE	Department of Environment
EPER	European Pollutant Emission Register
GAC	Granular Activated Carbon
HR	High Range
IOD	Biotoxicity
KTU	Kerosene Treating Unit
LPG	Light Petroleum Gas
OG	Oil and Grease
PAC	Powdered Activated Carbon
PTFE	Polytetrafluoroethylene
TOC	Total Organic Carbon
TSS	Total Suspended Solid

1 INTRODUCTION

1.1 Motivation and Statement of Problem

Wastewater from the petroleum refining industry typically has high chemical oxygen demand (COD) and oil-grease (OG) concentration, which brings harm to the environment, if it is released to the water bodies without treatment. The wastewater needs to meet the specification and requirement of Malaysian's Department of Environment (DOE) before being released to the environment. According to Environmental Quality for Sewage and Industrial Effluent Regulations 1979 Third Schedule (2012), the acceptable conditions for discharge of Industrial Effluent of Standard B, for OG concentration in wastewater is 10 mg/L and for COD concentration in wastewater is 100 mg/L.

Spent caustic is one of the types of wastewater in the petroleum refining industry. Spent caustic is used caustic soda or famously known as sodium hydroxide. It is widely used in petroleum refinery industry and petrochemical industry as scrubbing solutions for the removal of acidic components such as naphthenic acid, hydrogen sulphide and cresylic acids from the refined product stream (Kumfer, Felch and Maugans, 2010). Spent caustic is generated from refinery units such as Kerosene Treating Unit (KTU) in the petroleum refining industry. Raw kerosene uses caustic soda to remove hydrogen sulphide or mercaptans to produce commercial kerosene and jet fuel (Heidarinasab and Hashemi, 2011). Spent caustic from the KTU have high COD concentration, ranging from 50 000 to 150 000 mg/L (Felch, Clark and Kumfer, n.d.). This is because wastewater that contains spent caustic has a high sulphide concentration which is known as strong oxidant and other chemicals such as mercaptans, cresylic acid and sodium salts of naphthenic (Kumfer et al., 2010). However, there are not many reliable resources about the amount of oil and grease concentration that may contain in spent caustic. There are some possibilities that there are some kerosene carryover which contributes to high oil and grease concentration in the spent caustic wastewater. Releasing of untreated spent caustic brings harm to the environment. According to European Pollutant Emission Register (EPER) and Nationalencyclopedia (2010), a high COD concentration in the water may signify an oxygen deficiency, which brings harm to fish and other aquatic species that need oxygen to live (as cited in *Chemical Oxygen*

Demand (COD-Cr), n.d.). Besides that, if wastewater that contains high oil and grease concentration is discharged into water bodies, it leads to the formation of oil layer which causes significant pollution problem such as reduction of light penetration and photosynthesis (Alade, Jameel, Muyubi, Abdul Karim and Alam, 2011). Alade et al. (2011) also stated that it will prevent oxygen transfer from atmosphere to water bodies where it leads to decreased amount of dissolved oxygen at the bottom of the water and this will adversely affect the survival of aquatic life in the water.

Thus, several treatment processes of spent caustic where it focuses on the reduction of COD and other harmful chemical have been developed such as wet air oxidation, chemical reagent oxidation, catalytic oxidation, incineration, chemical precipitation and neutralization (Veerabhadraiah, Malika and Jindal, 2011). This study aims to treat spent caustic by using coagulation and flocculation method. According to Leopold and Freese (n.d.), coagulation is destabilization or charge neutralization reaction, whilst flocculation is the bridging of the destabilized particles to form larger particles. Coagulation and flocculation have been widely known to reduce turbidity and controls pH of the wastewater, but not many have tested its effectiveness to reduce COD and OG concentration. Besides that, this study also hoped to provide treatment alternatives and to widen the varieties for treatment of spent caustic in the petroleum refinery industry.

1.2 Objectives

The following are the objective of this study:

- To study the reduction of chemical oxygen demand (COD) and oil-grease (OG) concentration of spent caustic from Kerosene Treating Unit (KTU) at petroleum industry wastewater treatment plant by using coagulation and flocculation method.

1.3 Scope of Study

The following are the scopes of this research:

i) To analyse the COD and OG concentration in wastewater that contains spent caustic from KTU at a petroleum refinery company by using spectrophotometer and liquid-liquid partition-gravimetric method respectively.

ii) To use coagulation and flocculation method to treat the spent caustic wastewater samples.
iii) To find the best and suitable concentration of coagulant and flocculant based activated carbon in treating the wastewater samples, by using Jar test method.
iv) To compare the performance of the coagulant and flocculant based activated carbon in terms of its effectiveness in reducing COD and OG concentration.
v) To analyse the COD and OG concentration in treated spent caustic wastewater.

1.4 Main Contribution of This Study

The following are the contributions of this study:

i) The effectiveness of using chemical coagulation and flocculation method to reduce COD and OG concentration in spent caustic wastewater specifically from KTU tank can be determined.
ii) The best or suitable concentration of coagulants also can be determined by treating spent caustic wastewater specifically from KTU tank.
iii) This work also will add some varieties and options in treating spent caustic from KTU tank.

1.5 Organization of This Thesis

The structure of the rest of the thesis is outlined as follows:

Chapter 2 presents the literature review of this study. It started with the introduction of spent caustic where it generally describes the types of spent caustic, typical spent caustic composition and where does the spent caustic come from. This chapter also introduces COD, where it describes the major oxidants used in COD determination and the reactions behind the determination of COD. This chapter continues with the introduction of OG. After that, this chapter continues with the treatment method of spent caustic, where the advantages and disadvantages of commonly used spent caustic treatment have been listed. This chapter also introduced coagulation and flocculation method that have been used for the treatment of spent caustic in this study. Some brief reviews on the primary coagulant and coagulant aid have been presented in this chapter.

Chapter 3 talks about the material and methodology that have been used in this study. The chapter started off with an overview of the chapter and brief introduction about the

chapter. This chapter will brief about the chemicals, the spent caustic wastewater samples and also the analysis of the samples. Method to prepare the stock solution and also method to carry out the jar test will be explained as well.

This study continues with Chapter 4, where the results and discussions of this study are presented.

Last but not least, Chapter 5 presents about the conclusion and recommendation of this study.

2 LITERATURE REVIEW

2.1 Chapter Overview

This chapter introduces spent caustic wastewater. It also shows some previous study on spent caustic and the treatment method of spent caustic such as wet air oxidation. This chapter also reviews about the coagulation and flocculation method that are used to treat spent caustic wastewater from the KTU tank.

2.2 Introduction to Spent Caustic

Caustic soda or generally known as sodium hydroxide are used in the petroleum refining industry and the petrochemical industry as scrubbing solutions. Almost 85% by volume of the spent caustic is produced continuously in the treatment of kerosene (Huaman, Villar, Felch, Maugans and Olsen, 2008). According to "Analysis of Oxygen in Wet Air Oxidation of Spent Caustic Effluents" (n.d.), spent caustic typically comes from the production of ethylene and the oil refining process, where aqueous sodium hydroxide was used for the scrubbing of cracked gas and for the extraction or treatment of acidic impurities, such as hydrogen sulphide, mercaptans and organic acids in hydrocarbon streams. Maugans, Howdeshell and De Haan (2010) described that caustic soda was used in ethylene plants in the petrochemical industries to remove acid gases, hydrogen sulphide (H_2S) and carbon dioxide (CO_2) from the ethylene gas. In the petroleum refining industry, caustic soda was regularly used to remove H_2S and organic sulphur compounds from hydrocarbon streams (Sipma, Svitelskaya, van der Mark, Pol, Lettinga, Buisman and Janssen, 2004). Once the caustic soda has reacted and removed undesired chemicals from the streams, spent caustic is generated.

Generally, there are three types of spent caustic which are sulfidic spent caustics, cresylic spent caustic and naphthenic spent caustics. Sulfidic spent caustics produced from the caustic scrubbing of ethylene or light petroleum gas (LPG) products that contain high concentrations of sulfides and mercaptans (Kumfer et al., 2010). Cresylic or phenolic spent caustics produced from the caustic scrubbing of cracked gases or gasoline that contains phenols, cresols and xylenes with sulfides (Veerabhadraiah et al., 2011). Naphthenic spent caustic produced from the caustic scrubbing of kerosene and

diesel products that contain high concentrations of polycyclic organic compounds such as naphthenic acids (Kumfer et al., 2010). The main focus of this study is naphthenic spent caustic which comes from the KTU. In the KTU, the raw kerosene is pre-washed with 1.5-2% solution of caustic soda to neutralize both the hydrogen sulfide (H_2S) and the naphthenic acids that present in the raw kerosene (Prakash, 2003). The scrubbing process of raw kerosene by caustic soda are necessary to meet the acidity, mercaptan and other specifications required for upgrading raw kerosene to jet fuel products which is commercial kerosene, that are used by air transportations (Mohamadbeigy, Bayat and Forsat, 2006).

Spent caustics generally have different compositions that depended on the scrubbing process. Table 2-1 shows the typical chemical characteristics of three types of spent caustic.

Table 2-1: Typical spent caustic composition by Huaman et al.(2008)

	Reported as (g/L)	Sulphidic Spent Caustics	Naphthenic Spent Caustics	Cresylic Spent Caustics
Chemical Oxygen Demand, COD	O_2	7-110	50-100	165-230
Total Organic Carbon, TOC	C	0.02-4	11-25	23-60
Sulphide	S	2-53	<0.001	0-64
Sulphite	S	0.002-0.48	0.004-0.009	0.8-1.6
Mercaptans	CH_3SH	0-28	<0.03	0-5.4
Thiosulphate	S_2O_3	0-3.7	0.07-0.13	10-12
Iron	Fe	0.005-0.025	0.025-0.03	0.025-0.03
Total Phenols	C_6H_6O	0.003-0.02	2-10	14-20

Spent caustic solutions have high chemical oxygen demand as a result of all dissolved organics present in the spent caustic ("Acids and Caustic from Petroleum Refiining Category", 2009). They also added that the spent caustic solution has high alkalinity and corrosivity that may contribute to health and environmental hazards. According to "Analysis of Oxygen in Wet Air Oxidation of Spent Caustic Effluents" (n.d.), spent caustic is highly corrosive, have high contaminants, have a significant odor source and therefore disruptive to the operation of any downstream biotreatmnet facility and an environmental hazard that needs processing. In this study, chemical oxygen demand (COD) and oil-grease (OG) of spent caustic are being emphasized.

2.3 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) in spent caustic is one of the chemical characteristic that being tested in this study. COD has been one of the important parameters in the wastewater treatment. According to Boyles (1997), chemical oxygen demand is defined as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. Boyles (1997) added that the chemical oxygen demand test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to carbon dioxide (CO_2) and water (H_2O). The reaction mechanism can be summarized in equation (2.1):

$$\text{Organic carbon + Oxidant} \longrightarrow CO_2 + H_2O \qquad (2.1)$$

There are many chemicals that have been used as a strong oxidant in COD test such as potassium permanganate ($KMnO_4$), cerium (IV) sulphate ($Ce(SO_4)_2$), potassium thiosulphate (K_2S_2O), potassium iodate (KIO_3), oxygen (O_2), potassium dichromate ($K_2Cr_2O_7$), manganese (III) sulphate ($Mn(SO_4)_3$). Each of the major oxidants used in COD determination have their own advantages and disadvantages, which can be summarized in table 2-2.

Table 2-2: Advantages and disadvantages of major oxidants used in COD determination by Boyles (1997)

Oxidant	Advantages	Disadvantages
$KMnO_4$	• Stable for several months, MnO_2 must be excluded • Is used in acidic, neutral and basic media • Manganese is a non-hazardous metal	• Relatively slow-acting and is not quantitative • Results may depend upon sample size • Does not oxidize volatile acids or amino acids • Incomplete oxidation of organic compounds • Unstable in solution: Forms MnO_2 precipitate which catalyses reagent spending decomposition.
$Ce(SO_4)_2$	• More complete oxidation of organic compounds	• Incomplete oxidation of many organic

	• More stable than $KMnO_4$	compounds than $KMnO_4$ • Poor reproducibility • Photometric measurement at 320 NM where incompletely oxidized organic compounds interfere • Relatively expensive
K_2S_2O	• Oxidizes many organic nitrogen-containing • Widely used with TOC instrumentation	• Requires elaborate equipment compounds more completely than other oxidants • More labor intensive • Relatively unstable
KIO_3	• Strong oxidant	• Difficult to use • Questionable accuracy
O_2	• Oxygen consumption measured directly	• Elaborate equipment required
$K_2Cr_2O_7$	• Accomplishes a complete oxidation when used with a catalyst and a two-hour digestion period. • Stable at room temperature when protected from exposure to light	• Some organic compounds are only partially oxidized • Some organic compounds such as pyridine are not oxidized • There can be interference from inorganic pollutants, mainly chloride ions • Carcinogenic
$Mn(SO_4)_3$	• One hour digestion period • Correlates very well with Dichromate COD and BOD test results • Is not photosensitive • Is stable at room temperature • Reagent contains no hazardous metals and generates no hazardous metal waste	• Oxidizes approximately 80% oxidation of most organic compounds • Interference of most organic compounds, the reaction temperature is limited by thermal decomposition of the oxidant.

The strong oxidants used in this work are potassium dichromate ($K_2Cr_2O_7$). The dichromate ions ($Cr_2O_7^{-2}$) form orange colored solutions which will then reduce by organics to chromic ions (Cr^{3+}), forming a green solution (Roby, 2007). The reaction can be summarized in equation (2.2).

$$\underset{\text{(Orange)}}{\text{Organics} + Cr_2O_7^{-2}} \longrightarrow \underset{\text{(Green)}}{Cr^{3+}} \qquad (2.2)$$

Spent caustic wastewater specifically from KTU tank has high COD and possibly high OG concentration as well. Felch et al. (2012) have reported that spent caustic wastewater from the KTU tank have high COD concentration ranging from 50 000 to 150 000 mg/L, which is very high when compared to the regulation of the Department of Environment, Malaysia that permits only 100 mg/L of COD concentration in wastewater to be released to water bodies. According to Sipma et al. (2004), the formation of elemental sulphur in spent caustic wastewater contributed to high COD concentration. Hariz, Halleb, Adhoum and Monser (2013) also stated that the high concentrations of sulphur compound resulting in high concentrations of COD in spent caustic wastewater.

COD is an important parameter for wastewater or surface water testing as it gives information about the degree of water pollution by organic material ("Chemical Oxygen Demand of Water", n.d.). Besides that, "Chemical Oxygen Demand" (n.d.) emphasized that COD measurements are extremely useful to those concerned with water quality since they represents the amount of oxygen necessary for the aerobic biological oxidation of the organics in water sample to carbon dioxide (CO_2) and water (H_2O) if it is assumed the organics are biodegradable. In addition, COD can be related to Total Organic Carbon (TOC) and its value is about 2.5 times Biological Oxygen Demand (BOD) value ("Experiment On Determination of Chemical Oxygen Demand", n.d.). Besides that, the determination of COD was preferred than the determination of BOD as it only takes about 3 hour to determine the COD concentration n water and wastewater, compare to usual 5 days required for the measurement of BOD (Nanyang Technological University, 2004).

2.4 Oil and Grease (OG)

Choong, Paul and Jay (n.d.) have listed OG as one of the most important pollutants in the oil processing wastewater and are the most complicated to remove from the wastewater. The term "Oil and Grease" has become the popular term replacing the original term, which was "Fats, Oils and Grease", although both terms refer to the same wastewater constituents ("Understanding Laboratory Wastewater Tests: I. Organics", n.d.). OG are defined as any material recovered as a substance soluble in the solvent *(Standard Methods for The Examination of Water and Wastewater*, 2005). According to "Understanding Oil & Grease" (2012), the two main components of OG, which is petroleum based hydrocarbons, that being referred as nonpolar material and fatty compounds of animal or vegetable origin. Irwin, Mouwerik, Stevens, Seese and Basham (1997) have emphasized that OG includes not only petroleum oils but also vegetable oils, natural oils, some sediments, biota and decaying life forms that have high natural oils lipids. Alade et al. (2011) have stated that the oil contaminated wastewater comes from varied sources such as crude oil production, oil refinery, petrochemical industry, metal processing, compressor condensates, lubricants and cooling agents, car washing and restaurants. Table 2-3 shows the OG concentration from several industry:

Table 2-3: Oil and grease concentration from several industries by Cheryan (1998)

Industrial Sources	Oil and Grease Concentration (mg/L)
Food Processing	3800
Food Processing (Fish)	13700
Can Production (Forming)	200000
Wool Scouring	12200
Tanning Waste, Hide Curing	40200
Metal Finishing	6000
Petroleum Refinery	3200
Steel-Rolling Coolant	48700
Aluminium Rolling	5000

According to "Understanding Laboratory Wastewater Tests: I. Organics" (n.d.), there are three methods to measure oil and grease concentrations in wastewater which is liquid-liquid partition gravimetric method, the partition-infrared method and the Soxhlet extraction method. The general description of these method can be found in table 2-4.

Table 2-4: Oil and grease test method by Standard Methods for The Examination of Water and Wastewater (2005)

Test Method	General Descriptions
Liquid-Liquid Partition Gravimetric Method	• Dissolved or emulsified oil and grease is extracted from water by intimate contact with an extracting solvent, such as n-hexane. • Have an average recovery of 93% and standard deviation of 8.7%.
Partition-Infrared Method	• Uses trichlorotrifluoroethane as extraction solvent that allows absorbance of the carbon-hydrogen bond in the infrared to be used to measure oil and grease concentration. • Have an average recovery of 99% and standard deviation of 1.4%..
Soxhlet Extraction Method	• Soluble metallic soaps are hydrolyzed by acidification. Any oils and solids viscous grease present are separated from the liquid samples by filtration. • After extraction in a Soxhlet apparatus with solvent, the residue remaining after solvent evaporation is weighed to determine the oil and grease concentration. • Have an average recovery of 98.7% with a standard deviation of 1.86%.

They also added that oily wastewater, which means wastewater that contains high oil and grease concentration, contains toxic substances such as phenols, petroleum hydrocarbons, which are inhibitory to plant and animal growth, equally mutagenic and carcinogenic to human being. There are no data recorded for OG concentration in spent caustic wastewater. However, there is possibility that there is some kerosene carryover which contributes to high OG concentration in the spent caustic wastewater.

2.5 Treatment Method of Spent Caustic

There are some treatment method that can be used to treat spent caustic such as chemical precipitation, chemical reagent oxidation, incineration, wet air oxidation and neutralization (Veerabhadraiah et al., 2011). And of course, each of these treatment methods has its own pros and cons. Kumfer et al. (2010) stated that the three most

common methods for treating spent caustic wastewater are wet air oxidation and acid neutralization, which both followed by biological treatment or biological treatment without pre-treatment. According to Veerabhadraiah et al. (2011), the wet air oxidation method is the most widely used methods in the treatment of spent caustic because of its high treatment efficiencies, minimal air pollution and no sludge generation. The process flow diagram of a wet air oxidation process can be found in figure 2-1.

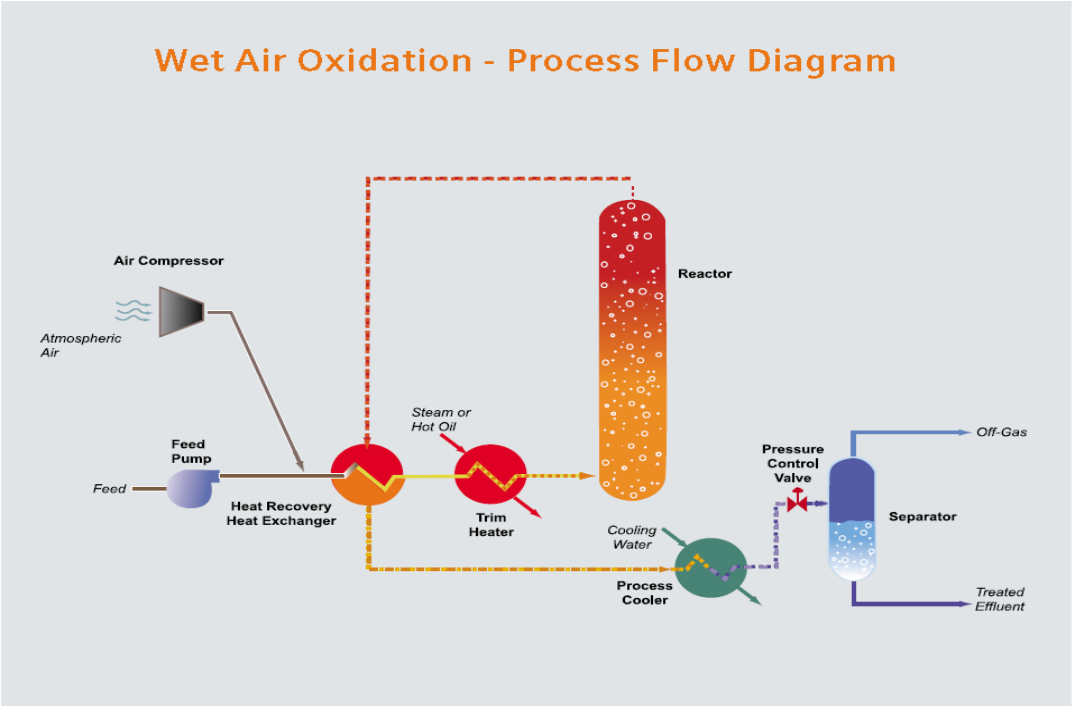

Figure 2-1: Wet air oxidation process by Felch et al. (2012)

However, this treatment process requires high pressure and high temperature and thus increasing its operating costs. Same goes to incineration method, which is a gas phase oxidation process that operates at much higher temperature that result in high operating costs (Veerabhadraiah et al., 2011). The advantages and disadvantages of the commonly used treatment process of spent caustic wastewater are listed in table 2-5.

Table 2-5: Advantages and disadvantages of commonly used spent caustic treatment by Veerabhadraiah et al. (2011)

Treatment Method	Advantages	Disadvantages
Chemical Oxidation	• Complete oxidation of sulphides • Low capital expenditures	• High peroxide consumption • Its availability in proximity may be an issue
Fenton Oxidation	• Oxidation of organics • Low capital expenditures	• High peroxide consumption • Its availability in proximity may be an issue • Unsuitable for sulphide removal • Handling of corrosive sulphuric acid • Generates chemical sludges
Chemical Precipitation	• Complete removal of sulphides • Removes emulsified oil and total suspended solids • Can be applied in existing flotation units • Low Capital expenditure	• Need for in-situ generation of chemicals • High chemical consumption • Large chemical sludge generation • Handling of corrosive chemicals • Occupation risk of chlorine gas leaks
Neutralization	• Recovers valuable phenol/organic	• High capital and operational expenditures for sulphide removal with add-on stripping and acid gas handling systems • Handling of corrosive sulphuric acid • Odour issues
Low Pressure Wet Oxidation	• Conversion of sulphides to thio sulphates, reducing biotoxicity (IOD)	• Partial oxidation which contributes to low BOD and COD reduction

	• Plant air may meet air supply needs	• Does not target organics; foaming potential • High capital expenditures which require offgas treatment
Middle Pressure Wet Oxidation	• Conversion of sulphides to sulphates • Partial oxidation of organics	• Does not completely oxidize organics • High capital and operational expenditure which needs off gas treatment • Middle pressure steam needs, which will lead to foaming potential
High Pressure Wet Oxidation	• Complete oxidation of sulphides or organics • No further offgas handling required	• High capital and operational expenditures • High pressure steam is needed
Catalytic Wet Oxidation	• Same as wet oxidation but reduced temperature and pressure • Enhanced thiosulphate oxidation	• High capital and operational expenditures • Catalyst handling
Incineration (Thermal Oxidation)	• Complete oxidation of sulphides and organics to sulphates and carbon dioxide and water • Can use waste oil or vent gases as fuels • May allow direct disposal	• High operational expenditure, if fresh grade fuels are used • Waste fuels may need special injector r atomizer • Sulphates and carbonates crystals formation need bulk and fine solids removal

According to Kolhatkar and Sublette (1996), spent sulphidic caustics are mostly sent off-site for commercial recovery or reuse, for example in pulp and paper mills, for treatment by wet air oxidation or for disposal by deep-well treatment. There are numerous studies of wet air oxidation on spent caustic wastewater (Fortuny, Font and Fabregat, 1998; Hosseini, Horvath, Schay and Szeles, n.d.; Oliviero, Wahyu, Barbier,

Duprez, Ponton, Metcalfe and Mantzavinos, 2003). However, there are no studies on coagulation and flocculation method for the treatment of spent caustic wastewater specifically from KTU tank. In this study, coagulation and flocculation method are used to treat spent caustic wastewater, by reducing the COD concentration and the OG concentration in the spent caustic wastewater.

2.6 Coagulation and Flocculation

In this study, coagulation and flocculation method are used to treat spent caustic wastewater by reducing its COD and OG concentration. Coagulation is the process by which the change from a liquid to a thickened, curd-like, insoluble state by some kind of chemical reaction, whilst flocculation is the process by which small particles of fine soils and sediments aggregate into larger lumps (Safferman, n.d.). There are three steps involved in this coagulation and flocculation process, which is the flash mix, coagulation and followed by flocculation ("Lesson 4: Coagulation and Flocculation", n.d.). Coagulation and flocculation methods are common practice in the treatment of drinking water by removing colloidal particles, which originates from clay, microscopic organisms, municipal waste, color compounds and organic matter that causes high turbidity in water (Safferman, n.d.). There are generally four mechanisms occurring in coagulation process which is enmeshment, adsorption, charge neutralization or destabilization and complexation or precipitation (Pernitsky, 2008). The coagulation reaction mechanism from Pernitsky (2008) can be summarized in figure 2-2.